

ELASTOMER TOUGHENED RADIATION CURABLE ADHESIVES

FIELD OF THE INVENTION

The present invention pertains to radiation curable adhesives prepared
5 using vinyl or propenyl ether monomers.

BRIEF DESCRIPTION OF RELATED TECHNOLOGY

Adhesives containing (meth) acrylate or cyanoacrylate monomers and
polymeric toughening agents are described in e.g. US 4440910 (O'Connor), US 5340873
10 (Mitry), and US 6225408 (Huang et al.).

Vinyl ethers are reported as mold release agents in compositions with
thermoplastic resins in US 4438234 (Rosenquist, et al.).

Curable vinyl ether formulations have been reported, primarily as coating
formulations.

15 Release coating formulations employing vinyl ether monomers are
described in US 5314929 (Crivello, et al.).

US 5139872 (Lapin, et al.) describes optical fiber coating formulations
based on vinyl ethers.

US 5567858 (Crivello) and US 5486545 (Crivello) describe
20 multifunctional propenyl ethers said to be useful as coatings, sealants, varnishes and
adhesives.

US 4388450 (Crivello) describes aromatic polyvinyl ethers and heat
curable molding compositions obtained therefrom. US 5070117 (Klemarczyk et al)
describes aromatic vinyl ethers, compositions thereof and methods of making same.

25 While, in some of these cases, vinyl and/or propenyl ether monomer
compositions are said to be utilizable as adhesives, they are generally unsuitable as such
since they react very rapidly, discoloring and disrupting substrate/adhesive interfaces,
have poor cure through depth, low viscosity, and poor toughness. Heretofore the use of
elastomer polymers in compositions of cationically polymerizable vinyl or propenyl
30 ether monomers has not been described.

SUMMARY OF THE INVENTION

The invention pertains to light curable adhesive compositions employing an α,β -olefinically unsaturated ether monomer such as a vinyl ether or propenyl ether monomer. The compositions of the invention give a less vigorous reaction, have higher viscosities, provide better cure through depth and provide better cured toughness than prior art radiation curable compositions prepared from such monomers. These properties make the inventive compositions much more suitable as adhesives than previous formulations embodying such monomers.

In one aspect, the invention is a radiation curable adhesive composition comprising:

- a) an α,β -olefinically unsaturated ether monomer component consisting of one or more compounds having the formula:



where R is an n-valent carbon-linked organic group R¹ is H or a monovalent carbon-linked organic group, suitably H or alkyl such as methyl, and n has a value of 1 or more,

- b) an elastomeric polymer having a tensile strength at break of greater than 1500 psi (10342 kPa), and an elongation at break of greater than 100%, and
- c) a cationic photoinitiator.

In another aspect, the invention is a method of bonding comprising:

- A) applying a composition as described above to a substrate,
- B) joining a second substrate, at least one of the substrates being transmissive to energy effective to activate the photoinitiator, and
- C) transmitting energy effective to activate the photoinitiator through said transmissive substrate to the composition to effect cure of the composition.

Bonded assemblies produced from the inventive adhesive formulations represent a further aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

All published documents, including all US patent documents, mentioned

anywhere in this application are hereby expressly incorporated herein by reference in their entirety. Any copending patent applications, mentioned anywhere in this application are also hereby expressly incorporated herein by reference in their entirety.

The compositions contain a an α,β -olefinically unsaturated ether

- 5 monomer component consisting of one or more compounds having the formula:



where R is an n-valent carbon-linked organic group R¹ is H or a monovalent carbon-linked organic group, n has a value of 1 or more, suitably 1 to 100, more typically 1-6.

Examples of suitable R and R' groups include 1-40 carbon aromatic or aliphatic

- 10 hydrocarbon groups, especially saturated linear, branched or cyclic aliphatic hydrocarbon groups; polyethers; cycloethers, for instance polysaccharide residues; residues of hydroxyl terminated urethane oligomers; and residues of hydroxyl terminated polyesters. In some embodiments R' may be H or an alkyl group of 1-10 carbon atoms, especially H (i.e. a vinyl ether), or methyl (i.e. a propenyl ether). Suitably the an α,β -olefinically
15 unsaturated ether monomer of formula I is employed in the composition in an amount of from about 20% to about 98% by weight of the composition.

Examples of specific vinyl ethers which may be utilized in the inventive compositions include butyl vinyl ether, hydroxy butyl vinyl ether, cyclohexyl vinyl ether, phenoxy vinyl ether, 2-ethylhexyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, and

- 20 octadecyl vinyl ether; the divinyl ethers of hexanediol, cyclohexane dimethanol, triethylene glycol, bisphenol A, alkoxylated bisphenol A and tetraethylene glycol; di and trivinyl ethers of glycerol or trimethylolpropane; and the di, tri or tetravinyl ethers of pentaerythritol. Further examples of such compounds may be found in US 4388450 (Crivello); US 5139872 (Lapin et al) and US 5314929 (Crivello et al).

- 25 Examples of propenyl ethers include 1,2-dipropenoxyethane, 1,4-dipropenoxybutane, 1,6-propenoxyhexane, 1,3-dipropenoxypropane, 1,4-cyclohexanedimethanol dipropenyl ether, 1,4-cyclohexane dipropenyl ether, 1,2-dipropenoxypropane, 1,10-dipropenoxydecane, 1,8-dipropenoxyoctane, 1,2,3-tripropenoxypropane, 1,2,3,4-tetrapropenoxybutane, sorbitol hexapropenyl ether,
30 trimethylolpropane triprenyl ether, pentaerythritol tetrapropenyl ether, 1,2-dipropenoxyxyclopentane, 1,3-dipropenoxyperfluoropropane, diethyleneglycol

dipropenyl ether, tetraethyleneglycol dipropenyl ether, and 3,4-dipropenoxytetrahydrofuran. The products may consist of pure isomers or mixtures of cis and trans isomers. Further examples of such compounds may be found in US 5567858 (Crivello) and US 5486545 (Crivello).

5 The compositions of the invention also include an elastomeric polymer toughener, or mixture thereof. For purposes of the present invention the elastomeric polymer toughener may be characterized as one having a tensile strength at break of greater than 1500 psi (10342 kPa), preferably greater than 2000 psi (13790 kPa), and an elongation at break of greater than 100%, preferably greater than 200%. The toughening
10 polymer will typically, but always be a block copolymer, including terpolymer, with a Tg of one block segment below -20°C. Suitably the elastomeric polymer is one which is dissolvable or highly swellable in the vinyl ether or propenyl ether monomer utilized in the formulation. Examples of suitable polymer tougheners include acrylic rubbers, butadiene/acrylonitrile rubber, styrene/butadiene rubber, buna rubber, polyisobutylene,
15 polyisoprene, natural rubber, polyurethane rubbers, ethylene-vinyl acetate polymers, fluorinated rubbers, isoprene-acrylonitrile polymers, chlorosulfonated polyethylenes, homopolymers of polyvinyl acetate, etc. Preferred polymer tougheners include acrylic rubbers and millable polyurethane rubbers.

 The acrylic rubbers may be selected from a wide range of suitable
20 materials. Most frequently these rubbers are either: (i) homopolymers of alkyl esters of acrylic acid; (ii) copolymers of another polymerizable monomer, such as a lower alkene, with an alkyl ester of acrylic acid or with an alkoxy ester of acrylic acid; (iv) copolymers of alkyl esters of acrylic acid; (v) copolymers of alkoxy esters of acrylic acid; (vi) mixtures of any of the above (i)-(v). Other unsaturated monomers which may be
25 copolymerized with the alkyl and alkoxy acrylic esters include dienes, reactive halogen-containing unsaturated compounds and other acrylic monomers such as acrylamides.

The acrylic rubbers may also include (meth)acrylic acid esters in limited amounts, suitably copolymerized with an acrylate ester or with a lower alkene.

 The choice of the elastomer will, to a large degree, dictate various
30 properties and characteristics of the adhesive composition and such choices are easily determined through general experimentation and known methods within the art. It is

most effective to use elastomers whose molecular weight averages more than about 100,000, but any molecular weight greater than 5,000 would be expected to effect an improvement. As a principle of general guidance, the molecular weight should be high enough to produce toughening but not so high that the adhesive is very stringy and difficult to apply. It is also best to choose an elastomer whose Mooney viscosity (ML(1+4)) is between 20 and about 60, and whose glass transition temperature (T_g) is 15° C or less. These specific limitations are not absolute and various acrylic rubbers which do not fall within them may be within the scope of this invention.

The elastomeric polymer toughener used in the present invention can also be, for example, an A-B-A block copolymer wherein the A block is polymerized segment of styrene, alpha-methyl styrene, t-butyl styrene, or other ring alkylated styrene, acrylonitrile, methyl methacrylate, or a mixture of some or all of the above and the B block is an elastomeric segment having a low T_g such as that derived from a conjugated diene or copolymer thereof or an ethylene-propylene monomer. Commercially available examples include EUOPRENE SOL T 193A™ available from Enichem Elastomers Americas, Inc.

As an example of a millable polyurethane there are the MILLATHANE polymers such as MILLATHANE 66 and MILLATHANE 76, available from TSE Industries.

Other references describing copolymers which are suitable for use as tougheners include US 3496250 (Czerwinski), US 3655825 (Souder et al), US 3668274 (Owens et al) and US 3864426 (Salensky). Preferred commercially available copolymers which can be used as is or treated as described below include BLENDEX BTA III F, ACRYLOID KM 680, ACRYLOID KM 653, ACRYLOID KM 611, and ACRYLOID KM 330 copolymers, all of which are commercially available from Rohm and Haas Company, BLENDEX 101 copolymer, commercially available from Borg-Warner Corp., METABLEN C 223 copolymer, commercially available from M & T Chemicals, Inc., and KANE Ace-B copolymer, commercially available from Kaneka America Corp.

Liquid rubbers may also be employed. For instance, liquid olefinic-terminated elastomers as described in US 4223115 (Zalucha et al); US 4452944 (Dawdy); US 4769419 (Dawdy); US 5641834 (Abbey et al), US 5710235 (Abbey et al)

and WO 97/39074 (Lord Corp).

The rubber is preferably dissolved in the monomer. The preferred rubbers are solid materials which are preferably masticated on a mill prior to dissolution in the vinyl ether or propenyl ether monomers. Properties of the cured adhesive composition
5 will vary somewhat with the degree of mastication, the effects of which may be determined with routine experimentation for any given rubber polymer. The rubbers should show little or no sign of phase separation once fully dissolved in the monomer.

The toughener may optionally be treated with a deionized water or methanol wash.

10 The amount of toughener can be varied to suit particular applications. A high level of toughener increases the viscosity of the resulting adhesive. The concentration range of elastomeric polymer will suitably be from about 3 to about 50 percent by weight, preferably 5 to about 30 percent, and more preferably about 7 to about 25 % based on the weight of the composition. Mixtures of tougheners can be used if
15 desired.

The curable compositions of the present invention also include a cationic photoinitiator, suitably an onium salt represented by the general formula:



where R² is an aromatic radical, for instance aryl, alkaryl, and aralkyl groups, including
20 fused ring structures comprising an aromatic ring, which may be optionally substituted with a linear, branched or cyclic C₈ to C₂₀ radical of alkyl, alkylene, alkoxy alkyleneoxy, a nitrogen, oxygen or sulfur heterocyclic radical of 4 to 6 carbon atoms in the ring; or a mixture thereof, A⁺ is selected from the group of iodonium cation mono-substituted with C₁ to C₂₀ alkyl or aryl optionally substituted with C₁ to C₂₀ alkyl or alkoxy and
25 sulfonium cation di-substituted with C₁ to C₂₀ alkyl or aryl optionally substituted with C₁ to C₂₀ alkyl or alkoxy or a mixture thereof and X⁻ is a non-basic, non-nucleophilic anion, examples of which include SbF₆⁻, AsF₆⁻, PF₆⁻, BF₄⁻, ClO₄⁻, CF₃SO₃⁻ and the like. Examples of such cationic photoinitiators are diaryliodonium, triarylsulfonium, diaryliodosonium, triarylsulfoxonium, dialkylphenacylsulfonium and
30 alkylhydroxyphenylsulfonium salts. Syntheses of such onium salts are described in US 4219654 (Crivello); US 4058400 (Crivello); US 4058401 (Crivello) and US 5079378

(Crivello). Although various members of the series of onium salts indicated above may be used in the practice of this invention, those bearing the SbF_6^- anion are preferred.

Commercial aryl onium salt cationic photoinitiators include UVI-6974, from Dow Chemical and UVE 1014 and UVE 1016 from General Electric Co.

5 Other suitable cationic photoinitiators include η^5,η^6 -iron arene complex salt catalysts as described in US 4808638 (Steinkraus et al) at cols 5-6. These catalysts, characterized as "ferrocenium salt" catalysts include, for instance IRGACURE 261, [η^5 -2,4-cyclopentadien-1-yl][(1,2,3,4,5,6- η)(1-methyl ethyl)benzene]-iron (+)-hexafluorophosphate(-), sold by Ciba Speciality Chemicals.

10 An effective amount of the cationic photoinitiator is from about 0.01% to about 20% by weight.

The compositions are cured by transmitting energy effective to activate the photoinitiator to the composition, suitably by irradiation, typically with UV or visible light. Irradiation of substrates treated in accordance with the practice of the invention
15 can be achieved by the use of UV lamps such as mercury arc lamps (high, medium and low pressure), xenon arc lamps, high intensity halogen-tungsten arc lamps, microwave driven arc lamps and lasers. Additional means of irradiation which can be used are, for example, x-rays, ionizing irradiation using ^{60}Co γ -rays and electron beam irradiation. In some cases the compositions may also be curable by heat or by IR irradiation.

20 The inventive adhesives may be made sensitive to long wavelength UV and to visible light by the addition of photosensitizers, in addition to the cationic photoinitiators, as described in U.S. Pat. No. 4610952 (Crivello). Among such photosensitizers may be mentioned Michler's ketone, perylene, pyrene, anthracene, benzophenone, thioxanthone, 2-isopropylthioxanthone and phenothiazine.

25 In addition to the monomer, elastomeric polymer and photoinitiator components described above, the coating formulations may also include non-elastomeric polymers such as poly(methyl methacrylate), polystyrene, poly- α -methylstyrene, polyacenaphthalene, polyindene, polyphenols, and novolac resins. Inorganic fillers such as silica, talc, clay, barytes, hydrated alumina and glass, polyolefin or polyimide fibers
30 may also be included to provide desirable mechanical characteristics, provided that they are not supplied in sufficient amount to preclude sufficient light penetration to the

desired cure depth to effect cure initiation within a reasonable irradiation time.

The inventive compositions may also optionally contain other conventional additives e.g. to regulate storage stability, viscosity, surface wetting properties, to promote adhesion, and the like.

5

The invention is illustrated by the following non-limiting examples.

EXAMPLES

Formulations were prepared by mixing the components identified in Table 1, below, first dissolving the polymer component in the monomer component and then 10 adding the photoinitiator. The formulation viscosities, measured with Brookfield viscometer, spindle #28, 10 RPM, 25°C are also given in Table 1.

Table 1

Components	1	2	3
Monomer			
Triethylene glycol divinyl ether	80	80	90
Polymer			
Millathane 66	20		
Millathane 76		20	
poly(ethyl acrylate)			10
Photoinitiator			
Cryacure 6976	1.12	1.12	1.12
Viscosity (mPa.s, 25°C)	8500	3800	3650

The formulations were cured in 20 mil thick glass molds by irradiating a

25 Loctite Fusion LC-6 UV conveyor oven, equipped with a mercury lamp producing broad spectrum UVA output generating an intensity at the substrate of 1.664 W/cm², measured at 365 nm using a EIT UV power pack, yielding a power of 2.851 J/cm² per pass. The molds were passed through the conveyer 2 times for each side, for a total of four passes.

Tensile properties of the films produced in this way (averages of 5 samples each) are 30 reported in Table 2.

UV cured adhesive shear strengths were also determined for 1 inch x 1

inch (2.54 cm x 2.54 cm) polycarbonate first blocks bonded to second, same sized, blocks of polycarbonate or polyvinyl carbonate using a $\frac{1}{2}$ inch (1.27 cm) overlap, cured in a Loctite Zeta 7200 Medium pressure Hg UV oven for 30 sec by irradiating through the first polycarbonate block, and testing after 24 hrs. Adhesive shear strengths were
5 determined using a Tinus Mechanical tester equipped with a special fixture. Results of these tests are given in Table 2.

Table 2

Formulation	1	2	3
Film tensile strength	500	830	637
PC/PC Block Shear Strength	1794	1621	1503
PC/PVC Block Shear Strength	1533	557	493

These results demonstrate that the inventive formulations can function as
15 effective structural adhesives

The above examples and disclosure are intended to be illustrative and not exhaustive. These examples and description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the claims, where the term "comprising" means "including, but not limited to." Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims. Further, the particular features presented in the dependent claims can be combined with each other in other manners within the scope of the invention such that the invention should be recognized as also specifically directed
20 to other embodiments having any other possible combination of the features of the dependent claims. For instance, for purposes of claim publication, any dependent claim which follows should be taken as alternatively written in a multiple dependent form from all prior claims which possess all antecedents referenced in such dependent claim if such multiple dependent format is an accepted format within the jurisdiction (e.g. each claim
25 depending directly from claim 1 should be alternatively taken as depending from all previous claims). In jurisdictions where multiple dependent claim formats are restricted,
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the following dependent claims should each be also taken as alternatively written in each singly dependent claim format which creates a dependency from a prior antecedent-possessing claim other than the specific claim listed in such dependent claim below.